Appendix A

Invention Disclosure Document of Applicants Evidencing Conception of Invention of U.S. Patent Appln. No. 09/681,609

INVENTION DISCLOSURE

ROI Numbe[redacted]

Barrier Structures for Integration f High K Oxides with Cu and Al Electrodes

(1) State the PROBLEM or DEFICIENCY which is overcome by your invention:
Ferroelectric and other complex oxide thin films are commonly used with noble metal electrodes such as Au, Pt and Ir, or on other metal oxides such as RuO_x. This is for a variety of reasons, which include oxidation resistance, work function, and stability at high temperatures. These issues are particularly important for bottom electrodes, which must withstand the stress of high temperature and oxidizing conditions in thin film deposition processes. Unfortunately, such materials are expensive, of limited availability in semiconductor production environments, difficult to etch, and have relatively low conductivity (in the case of Pt in particular). In addition, Pt, for example, is highly permeable to Bi and Pb, making it difficult to use these elements in films for nonvolatile memories.

Copper would be a more desirable electrode material, as it is in increasing use in the semiconductor industry and has excellent conductivity. Unfortunately, it oxidizes rapidly in the high temperature oxidizing environment used to deposit complex oxide films, and may even oxidize at the interface when deposited as a top electrode. This interfacial layer is likely to roughen the interface between the dielectric and the metal, increasing leakage and loss. In addition, interreactions may occur between the copper and the dielectric oxide, forming poorly controlled interfaces which are likely to affect electrical properties. The same issues are present (in addition to low melting point of the metal) if these films are attempted with Al electrodes.

In example of this, low temperature growth of thin films of $SrBiTaO_3$ (SBT) has been performed at ATMI by MOCVD on Cu electrodes. In each case the parallel plate capacitors formed after application of top electrodes were found to be shorted and useless. In another example, Al top electrodes were deposited on perovskite $BaSrTiO_3$ thin films formed at ATMI by MOCVD on Pt bottom electrodes. The use of Al top electrodes caused shorting of all capacitors formed, while use of Pt top electrodes produced working capacitors.

In order to avoid these problems with use of complex oxide dielectrics with Cu and Al, barrier layers are needed. These barrier layers must be conductive, compatible with both the readily oxidized metal underneath (Cu or Al) and with the complex oxide layer on top, and survive at a

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relevant growth temperature, which may range from 300 to 700 °C depending on the material system. It may be necessary to use multiple layers for these barriers.

(2) Describe clearly the INVENTION, RESULTS, ADVANTAGES. (Make DRAWINGS when possible and DESCRIBE FULLY the invention and its OPERATION using REFERENCE NUMERALS to indicate elements.

In solving these issues mentioned above, we must first examine the layer in contact with the complex oxide layer. Some advantages and disadvantages of different candidates are discussed in Table 1, where (X)N refers to a number of related nitrides such as TaN, WN, W_2N, TiAlN, ZrN, NbN, HfN and ternaries including these materials such as NbAlN.

Table 1. A comparison of different potential dielectric contacting bottom electrode structures.

Structure	Compatibility	Cost	Conductivity	O - barrier	O-Bi resistance	Pb resistance
Pt	Very Good	High	Low	Good	OK	Poor
Ir	Very Good	High	Middle	Better	Best	OK
Cu	Low (?)	Low	High	Poor (?)	Poor (?)	Poor (?)
(X)N	Unknown	Middle	Middle	OK	OK (?)	OK (?)
(Ti,Al)N	Unknown	Middle	Middle	Best	OK (?)	OK (?)

By combining the strengths and weaknesses of these layers, we can consider a number of different stack combinations which might be suitable for barrier layer purposes. These possibilities, along with relative advantages and disadvantages, include (where Al could be used in place of Cu);

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Table 2. A comparison of possible electrode combinations, advantages and disadvantages.

Metal	Advantages	Disadvantages
Pt	Best known, Pt good template	O, Bi, & Pb permeable, low industry acceptance
Ir	Well known	Oxidize and form rough surface, low industry acceptance
IrO_2	Same as Ir	low industry acceptance
Cu	Common in industry	Strong oxide formation
Pt/Cu	Simple	May form oxide at Pt/Cu interface
Ir/Cu	Simple, Ir resists O, Bi, & Pb	May oxidize and form rough surface
IrO_2/Cu	Simple, as above and less roughening during high k deposition	May form Cu oxide at interface
CuO_x/Cu	Single material system	Copper oxide not a good barrier/template, poor conductivity or low dielectric constant
TaN/Cu	TaN well known, good Cu sticking	TaN will oxidize at BST growth temperature
TiAlN/Cu	TiAlN accepted in industry	Some oxidation at temperature, unknown Cu sticking
Pt/TiAlN/Cu	Pt good template	Pt not oxygen barrier, complex (3-layer)
Pt/IrO_2/Cu	Pt good template	IrO_2/Cu interface may oxidize, complex
Ir/IrO_2/Cu	Ir, IrO_2 good barriers, only one metal	IrO_2/Cu interface may oxidize, Complex (3-layer)
Ir/TiAlN/Cu	Ir protects TiAlN	Complex (3-layer); potentially form oxide at IrO_2/TiAlN interface
IrO_2/TiAlN/Cu	IrO_2 good barrier	Complex (3-layer)
IrO_2/Ir/Cu	As above, and oxide contacts oxide	Complex (3-layer)
IrO_2/IrO_x/Ir/Cu	As above, and could be made as a single graded process step	A more complex process step

The extent to which these advantages and disadvantages are relevant depends on the material system ($BaSrTiO_3$ or BST, $SrBiTaO_3$ or SBT and derivative oxides such as $BiTaO_3$, $PbZrTiO_3$ or PZT) used and the growth temperature. At low growth temperatures, for example, such as those around 350 to 450 °C which are used for amorphous SBT, a growth surface such as TiAlN may not be oxidized, while at higher temperatures, around the 600-650 °C which are used for perovskite BST, a more robust top layer may have to be used, such as IrO_2.

It is obviously preferable to use simpler systems (one or two layers) in preference to more complex (three or four layers) systems, for reasons of manufacturability. Minimal layers of precious metals or exotic materials in combination with primarily Cu or Al is also preferable, as

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this reduces cost and makes etching easier, since thick layers of resistant materials need not be rem ved.

Thus, our recommendations are as follows for particular material systems (note that any Cu containing combinations have not yet been tried). In each case, we would expect that the precious/exotic top layers would be comparatively thin relative to the Cu or Al layer, which would be the primary current carrying electrode for the device.

Material System	Growth Temperature	Recommended Electrode
BST (perovskite)	600-660 °C	Pt, Ir, Pt/Ir/Cu
BST (high Ti content, amorphous	540-620 °C	Ir/Cu, IrO_2/Cu
SBT (amorphous)	350-450 °C	Ir/Cu, TiAlN/Cu
PZT	450-600 °C	Ir, Ir/Cu, IrO_2, IrO_2/Cu

Where in place of TiAlN other nitride barrier layers such as those discussed earlier could be used. In addition, it is probably not desirable to deposit Ir directly on Si, as iridium silicides form readily. Thus some additional barrier should be used in these cases.

In example of use of a nitride electrode directly, we have deposited a PZT film on (Ti,Al)N directly, sample VZ1203 (Barry Chen). XRF analysis indicates that the resultant film was essentially TiO_x, very little Pb or Zr. That may be considered a good sign for Pb diffusion resistance of this barrier. One of the potential disadvantages of this system is that the surface of the nitride layer can become oxidized even if the layer is not permeable to oxygen diffusion. In the case of (Ti,Al)N, a poor-quality TiO_x/AlO_x surface layer may have been formed between the dielectric oxide and the barrier nitride. Thus, these materials may benefit from a nitride which is even more oxidation-resistant than (Ti,Al)N.

(3) Was this invention first conceived or first actually reduced to practice under government contract support? If so, what are the contract name and contract number?

No.

(4) Has there been any publication, public disclosure, or offer for sale, or are any contemplated? Provide details, especially dates.

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None to date, but we are contemplating using this information in a joint development program with Intel.

(5) Laboratory Notebook or Runsheet Number cross reference, including date(s).

None, developed in discussion in [redacted], now being documented.

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Appendix B

November 7, 2000 Email from Maggie Chappuis to Steven Hultquist, Relating to Preparation of Patent Application Directed to Invention

Steven Hultquist

From: mchappuis@atmi.com
Sent: Tuesday, November 07, 2000 4:42 PM
To: Steven Hultquist
Subject: New Patent Application for "Barrier Structures for Integration of High KOxides with Cu and Al Electrodes" ATMI File: 497

00-20.doc

ATMI, INC. COMPANY CONFIDENTIAL

Steven:

Please prepare an application draft directed to the disclosure in the attached ROI for "Barrier Structures for Integration of High K Oxides with Cu and Al Electrodes".

The inventors in the case are Gregory T. Stauf, Bryan C. Hendrix, Jeffrey F. Roeder and Ing-Shin Chen. The project code is OH0008

Appendix C

December 10, 2000 Email from Steven Hultquist to Oliver Zitzmann, Enclosing Draft of Patent Application Directed to Invention

Steven Hultquist

To: ozitzmann@atmi.com
Subject: Patent Application for ATM-497

December 10, 2000

Oliver -

Attached are the text and drawings of the patent application for ATM-497.

497_Application_120900.doc

Figures.doc

Steven